Liquid electrode plasma-optical emission spectrometry combined with solid-phase preconcentration for on-site analysis of lead

Liquid Electrode Plasma-Optical Emission Spectrometry Combined with Solid-Phase Preconcentration for On-Site Analysis of Lead

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Abstract

A relatively rapid and precise method is presented for the determination of lead in aqueous matrix. The method consists of analyte quantitation using the liquid electrode plasma-optical emission spectrometry (LEP-OES) coupled with selective separation/preconcentration by solid-phase extraction (SPE). The impact of operating variables on the retention of lead in SPEs such as pH, flow rate of the sample solution; type, volume, flow rate of the eluent; and matrix effects were investigated. Selective SPE-separation/preconcentration minimized the interfering effect due to manganese in solution and limitations in lead-detection in low-concentration samples by LEP-OES. The LEP-OES operating parameters such as acid concentration, applied voltage; on-time, off-time, pulse count for applied voltage; number of measurements; and matrix effects have also been optimized to obtain a distinct peak for the lead at λ_{max} = 405.8 nm. The limit of detection (3σ) and the limit of quantification (10σ) for lead determination using the technique were found as 1.9 and 6.5 ng mL^{-1}, respectively. The precision, as relative standard deviation, was lower than 5% at 0.1 μg mL^{-1} Pb, and the preconcentration factor was found to be 187. The proposed method was applied to the analysis of lead contents in the natural aqueous matrix (recovery rate: >95%). The method accuracy was verified using certified reference material of wastewaters: SPS-WW1 and ERM-CA713. The results from LEP-OES were in good agreement with inductively coupled plasma optical emission spectrometry measurements on the same samples. The application of the method is rapid (≤5 minutes, without preconcentration) with a reliable detection limit at trace levels.

Keywords

Lead; Solid-phase extraction; Selective separation; Preconcentration; LEP-OES; On-site analysis

1.0 Introduction

Lead (Pb), a ubiquitous element in nature, continued to be used in the manufacturing processes of pipes, solder, paint, cables, ceramics, and batteries due to its many desirable properties, e.g., malleability, low melting point, ability to form compounds, and so forth [1, 2]. However, Pb-exposure, even at a minute level, can cause neurodevelopmental disorders, cardiovascular malfunctions, impaired renal function, reduced fertility and adverse pregnancy outcomes, with confrontational impacts to the young children [3-6]. The guideline value for chemical hazards in drinking water from World Health Organization [7] and the directive from the Council of the European Union on the quality of water intended for human consumption [8] recommended a maximum admissible concentration of 10 $\mu g\ L^{-1}$ Pb [9]. Hence, stringent regulations regarding the use of Pb has been proposed [10], and development of analytical techniques with high sensitivity for detection of such a low Pb-concentrations in environmental matrices has gained critical interest.

Laboratory-based routine analyses for Pb are frequently performed using inductively coupled plasma optical emission spectrometry (ICP-OES) [11, 12], inductively coupled plasma-mass spectrometry [13], graphite furnace atomic absorption spectrometry [14], and flame atomic absorption spectrometry [15]. However, these techniques are time-consuming, require expensive and complex instrumentation, need substantial operating cost, while unsuitable for field analysis.

There are proposed techniques for on-site analysis of metals in aqueous matrices based on the principle of optical emission spectroscopy using electro cathode discharge [16], dielectric capillary barrier discharge [17], on-chip microglow discharge [18], and liquid electrode plasma (LEP) [19-22] systems. Liquid electrode plasma-optical emission spectrometry (LEP-OES) has attracted extensive attention to the field measurement application due to its integral advantages of simplicity, portability, low cost, high sensitivity, a minimum skill requirement in operation and use of a little amount of sample [23, 24]. In LEP-OES, a high-voltage DC pulse power is applied to the vapor-bubble generated from an electro-conductive liquid passed through a narrow-center micro channel to create LEP. The emission spectra of the discharged plasma are measured in a spectrometer according to its wavelength to quantify metal ions concentration in the liquid [21]. However, there are two drawbacks during the

application of LEP-OES for Pb measurement: (a) it is not sufficiently sensitive to detect Pb in low-concentration (≤1 μg mL^{-1}) sample [25]; and b) the quantitative detection of Pb is hindered when manganese (Mn) ion coexists in solution due to the relatively closer emission lines (Mn: 403.08 nm, Pb: 405.78 nm) [25, 26].

Selective preconcentration is a widely adopted pretreatment technique to overcome the deficiencies due to low detection limits as well as to minimize the impacts of interfering ions [27-29]. Among several preconcentration techniques, e.g. liquid-liquid extraction, co-precipitation, ion-exchange and solid-phase extraction (SPE), SPE is preferred more as it is sensitive, simple, faster, sample-saving and environment-friendly [2, 27, 30-32]. SPE method uses binding affinity between the element and both the solid-phase and eluent. The analyte is first captured within the solid-phase, which is later extracted using an appropriate solvent (known as, eluent) due to the comparatively higher affinity of analyte and eluent [24, 33, 34]. SPEs designed for molecular recognition technology (MRT), which employ 'host-guest' phenomenon to capture a target analyte, is useful in achieving desired selectivity [31, 35, 36]. The objective of present work is to develop a portable technique for quantitative on-site Pb-analysis combining selective preconcentration with MRT-SPE and measurement by LEP-OES. The unique point of the method is the rapid analysis of Pb with a detection limit at ppb level and affordable cost in resource-limited settings using LEP-OES, which has not been reported before.

2.0 Experimental

2.1 Materials

2.1.1 Instruments

The LEP-OES, commercially named as MH-5000 ultra-compact elemental analyzer (Model: S-2043; size: L 204 mm, W 105 mm, H 114 mm; weight: 1400 g including batteries; power supply: six AA size batteries or AC adapter) from Micro Emission Ltd. (Nomi, Japan) was used for analysis. The system is equipped with an emission quartz cuvette LepiCuve-C as a sample holder and LepiSuite LEP Analyzer software for data processing. It operates in wavelength ranges from 200 to 430 nm. The operating principle of the MH-5000 LEP-OES is shown in Figure S1 (see Supplementary information file).

An iCAP 6300 ICP-OES from Thermo Fisher Scientific (Waltham, MA) was used for the measurement of metals, for optimization experiments and verification of the measurements done with LEP-OES. The ICP-OES was composed of an EMT duo quartz torch, glass spray chamber and concentric glass nebulizer (operating conditions: RF power at the torch, 1.15 kW; plasma gas flow, 12 L min^{-1}; auxiliary gas flow, 1 L min^{-1}; nebulizer gas flow, 0.5 L min^{-1}; integration time, 30 s; replication, 3 times).

An automated TOSOH 8020 high-performance liquid chromatography system from Tosoh (Tokyo, Japan) was used to verify the concentration of ethylenediaminetetraacetic acid (EDTA) that was used as eluent. A GL-SPE vacuum manifold kit from GL Sciences (Tokyo, Japan) in combination with CAS-1 air pump from AS ONE (Osaka, Japan) was used for Pb-separation optimization experiments using mini-columns. An Arium Pro automated water purification system from Sartorius Stedim Biotech GmbH (Göttingen, Germany) was used to produce ultrapure water (resistivity >18.2 MΩ cm^{-1}). A Navi F-52 digital pH meter from Horiba Instruments (Kyoto, Japan) was used to measure solution pH.

2.1.2 Chemicals

Analytical grade reagents have been used throughout without further purification. The 1000 ppm standards of Pb, Mn, Li, Na, Mg, K, Ca, Sr and Ba from Kanto Chemicals (Tokyo, Japan) were used as stock solutions and for metal concentration measurements. The Anion mixed standard solution III containing Cl^-, Br^-, NO_2^-, NO_3^-, and SO_4^{2-} from Kanto Chemicals (Tokyo, Japan) was used to check the matrix effect due to anions. EDTA from Nacalai Tesque (Kyoto, Japan), and HCl, HNO_3, and NaOH from Kanto Chemicals (Tokyo, Japan) were used as eluents. The Scat 20X-PF alkaline detergent from Nacalai Tesque (Kyoto, Japan) and HCl (4 mol L^{-1}) were used for cleaning laboratory wares.

The source solutions were diluted using ultrapure water on a weight basis to prepare working solutions in the range of μg L^{-1} to μg mL^{-1}. The solution pH at ≤2 was achieved using 1 mol L^{-1} HNO_3, while the pH above that range for other working solutions was adjusted using 1 mol L^{-1} HNO_3 or NaOH. The 0.1 mol L^{-1} solutions of buffer reagents, namely 2-(*N*-morpholino)ethanesulfonic acid (MES) from Sigma-Aldrich (St. Louis, MO), 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES) from Nacalai Tesque (Kyoto, Japan), and *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) from MP

Biomedicals (Solon, OH) were used to maintain solution pH, respectively, ranged from 3 to 5, 6 to 8 and 9 to 10.

Certified reference materials (CRMs) of wastewaters: SPS-WW1 from Spectrapure Standards AS (Oslo, Norway) and ERM-CA713 from European Commission Joint Research Centre, Institute of Reference Materials and Measurements (Geel, Belgium) were used to check the accuracy of the method. Fortified samples of 'real' waters: tap water from the general utility supply of *Sakuramachi* residential area and Research Laboratory at Kakuma campus, Kanazawa University (Kanazawa, Japan), river water from Asano river (Kanazawa, Japan), and rain water collected from Sakuramachi (Kanazawa, Japan; collection date: 18-Sep-2016) were analyzed to validate the proposed method.

2.1.3 Solid-phase extraction systems

MRT-SPE systems commercially named as AnaLig Pb-01 (Pb-01), AnaLig Pb-02 (Pb-02) and AnaLig Pb-04 (Pb-04) from IBC Advanced Technologies (American Fork, UT) obtained via GL Sciences (Tokyo, Japan) were appraised for the preconcentration step. These MRT-SPEs (base support: silica gel; functional group: crown ether) are claimed to possess selectivity to Pb in complex matrices, have a mesh size between 60 and 100 and density of 0.4 g mL^{-1}.

2.1.4 Laboratory wares

Low-density polyethylene (PE) containers from Nalgene Nunc (Rochester, NY), screw-capped PE tubes from AS ONE (Osaka, Japan), polypropylene Jars from Tomiki Medical Instrument, (Kanazawa, Japan) and micropipette tips from Nichiryo (Tokyo, Japan) were used during experiments. Laboratory wares were cleaned before use by overnight soaking in Scat 20X-PF detergent followed by nightlong immersion in HCl (4 mol L^{-1}) while rinsing with ultrapure water after each of the above steps.

2.2 Methods

2.2.1 Measurement of an element using LEP-OES

Measurement of liquid samples using LEP-OES, equipped with quartz-made LepiCuve-C, included a pre-operational cleaning step using ultrapure water and ethanol. The LepiCuve contains two openings at the top, and ultrapure water was inserted using a syringe (1 mL)

through either one of the openings while removed via the other. The washing with ultrapure water was repeated for at least twice. Ethanol was then inserted and allowed to be air-dried. The solution heights in both chambers of the LepiCuve has been equalized using air-pressure via syringe.

The measurement of an aqueous sample using LEP-OES initiated with the following sub-steps: a) adjustment of the conductivity of sample solution; b) check the solution viscosity and bubbling extent, which were expected to be analogous to that of water; and c) identification of the distinct emission peaks for the target element.

The conductivity of Pb-containing sample solutions was adjusted using HNO_3 (0.1 or 1.0 mol L^{-1}) and maintained similar for standards and samples to attain precision in measurements. The LEP-OES operating parameters, such as applied voltage (700 to 1050 v; interval, 50 v), on-time (1 to 8 ms; interval, 1 ms), off-time (10 to 80 ms; interval, 10 ms), pulse count (10 to 110; interval, 20), and the number of measurements per spectra (3, 5, 6, or 10) has been varied. The objective was to amplify the emission peak intensity obtained at 405.782 nm using the default measurement conditions: applied voltage, 750 v; on-time, 3 ms; off-time, 40 ms; pulse count, 40. Each cycle of measurements include several pulses of applied voltage, denoted as pulse count, to the sample solution. One pulse count is equivalent to each set of on-time and off-time. The term *on-time* is used to designate the duration of each pulse of applied voltage, while the *off-time* is used to represent the interval period between the pulses.

The LepiCuve containing the sample (~40 µL per measurement cycle) was then placed within the apparatus as designated, and the LepiSuite LEP Analyzer performed the analysis according to pre-programmed measurement conditions. The optimized conditions for applied voltage, on-time, off-time, pulse count and the number of measurements per spectra have been determined from multiple experiments and employed for the LEP-OES analysis of Pb. An illustrated guide to set the sample in LepiCuve for measurement using the MH-5000 LEP-OES is shown in Figure S2 (see Supplementary information file).

The sample measurements were preceded by a standard curve preparation using solutions of varying concentrations of the target element (Pb in the current work) and a blank (HNO_3, 0.1 or 1.0 mol L^{-1}). In the current work, the interim washing steps during the analysis of metal-laden samples included an additional washing cycle using HNO_3 solutions identical to the blank.

2.2.2 Selective separation and preconcentration of lead for LEP-OES analysis

The Pb-01, Pb-02 and Pb-04 MRT-SPE systems are compared for selective Pb-separation efficiency from the aqueous matrix in terms of retention and recovery rates. The total SPE-treatment process consisted of several steps, such as, conditioning, sample loading, washing and elution. The retained fraction of loaded analytes in SPE ($C_{retained} = C_{initial} - C_{residual} - C_{wash}$; $C_{initial}$, analyte content in base solution, $C_{residual}$, residual analyte in solution after SPE treatment, C_{wash}, slackly-retained analytes that were recovered with wash solution) is compared to the $C_{initial}$ to calculate extraction rate. The recovery rate was calculated by comparing eluted analyte content ($C_{elution}$) from SPE with that of $C_{retained}$. The operating variables for MRT-SPEs, e.g., solution pH (1 to 8; interval: 1 pH unit), flow rates (0.3 to 10 mL min^{-1}), washing solvent (acid or water) and eluent (acid, base or chelator), were optimized using mini-columns (500 mg particles packed in 3 mL columns), followed by measurements using ICP-OES. A detailed protocol for the SPE-assisted separation treatment of aqueous waste matrix was reported elsewhere [37, 38].

The MRT-SPE options were compared based on the selectivity towards Pb and compatibility with variables, and the selected one was packed in polypropylene pipette tips (D 6 mm, L 45 mm) to prepare micro-columns with 20 mg of SPE particles. The optimized operating variables with mini-column were applied, followed by some adjustment in the eluent pH to facilitate the analysis with LEP-OES.

3.0 Results and Discussion

3.1 Optimization of LEP-OES parameters for lead measurement

3.1.1 Acid concentration and applied voltage

In the LEP-OES technique, the plasma is generated by applying a voltage in solution. Hence, a pre-adjustment of the solution viscosity equivalent to that of water and electrical conductivity similar to a solution of pH 0~1 is recommended [39]. A comparison of the resistance value of strong acids of pH 0 (1.0 mol L^{-1} HNO_3) and 1 (0.1 mol L^{-1} HNO_3) with that of Pb standards (1 to 5 µg mL^{-1}) in HNO_3 of similar concentrations, at the default measurement conditions of MH-5000 (voltage, 200 V; on-time, 2 ms; off-time, 40 ms; pulse count, 10), indicated a non-significant variation between standards and samples (Figure 1a).

The emission peak for an element should be distinguishable from the background peaks for quantitative accuracy in analysis, and the peak intensity is proportionally related to the applied voltage in LEP-OES [24]. The observed peak height (λ_{max} for Pb, 405.8 nm) was very low at the default standard conditions for Pb in 0.1 mol L^{-1} HNO_3 (voltage, 750 V; on-time, 2 ms; off-time, 40 ms; pulse count, 40) or Pb in 1.0 mol L^{-1} HNO_3 (voltage, 650 V; on-time, 2 ms; off-time, 40 ms; pulse count, 40). However, the solutions of Pb in 1.0 mol L^{-1} HNO_3 spilled off from LepiCuve when the applied voltage was ≥ 650 V for more than three simultaneous measurements, while 10 or more continuous measurements were possible for samples in 0.1 mol L^{-1} HNO_3. Therefore, the sample pH adjustment has been performed using 0.1 mol L^{-1} HNO_3 only to maintain the desired solution conductivity during further experiments. The changes in the peak intensity for Pb standards (1, 3 and 5 µg mL^{-1}) in 0.1 mol L^{-1} HNO_3 at different applied voltage in the range of 750 to 1050 v, while other parameters were fixed to default, were checked. The peak intensity for Pb at λ_{max} = 405.8 nm was gradually increased with higher applied voltage until 950 v followed by a decrease, which indicated 950 v as the optimized applied voltage for the Pb analysis (Figure 1b; see Figure S3 in the supplementary information file for the comparative spectra).

3.1.2 On-time, off-time and pulse count for applied voltage

The on-time and off-time for applied voltage are two other LEP-OES operating parameters that influence the emission peak intensity, and the correlation differs with the element to be measured rather than common proportional or reciprocal tendency [39]. The effect of varying on-time (1 to 8 ms) on the emission peak intensity at an optimized applied voltage (950 v) plus default conditions for Pb (3 µg mL^{-1}) in 0.1 mol L^{-1} HNO_3 (off-time, 40 ms; pulse count, 40) has been studied. The highest peak intensity was obtained for 5 ms on-time (Figure 2a; see Figure S4 in the supplementary information file for the comparative spectra).

The effect of off-time (10 to 80 ms) has been monitored keeping the on-time and applied voltage fixed at 5 ms and 950 v, respectively. The default pulse count of 40 for Pb (3 µg mL^{-1}) in 0.1 mol L^{-1} HNO_3 showed an initial increase in the emission intensity followed by a gradual decrease (Figure 2b; see Figure S5 in the supplementary information file for the comparative spectra). The variation in emission intensity was compared with the coefficient of variation (CV) (standard deviation (SD) of the emission intensity/mean × 100) to select the

suitable off-time. A higher emission intensity in correspondence with lower CV is suggested for the quantitative analysis of an element in MH-5000 [39], which was observed at 60 ms off-time.

Each cycle of on-time and off-time are considered as one pulse count of the applied voltage in LEP-OES measurements. The optimized applied voltage (950 v), on-time (5 ms) and off-time (60 ms) were used in combination with different pulse counts (10 to 110) for measurements of Pb (3 μg mL^{-1}) in 0.1 mol L^{-1} HNO_3. A lower CV value with higher emission intensity was observed for 90 pulse count (Figure 2c; see Figure S6 in the supplementary information file for the comparative spectra).

3.1.3 Number of measurements per spectra

One spectrum is equivalent to the one measurement result obtained after applying an optimized number of a pulse count, and the spectra produced after a predetermined number of iterative analysis of the same sample is known as one group [39]. The Mean, SD, and CV for the emission intensity values obtained for different group aggregates of 30 single measurements (*n*, number of measurements per group = 3, 5, 6, 10) were calculated for Pb (3 μg mL^{-1}) in 0.1 mol L^{-1} HNO_3 at λ_{max} = 405.8 nm obtained at pre-optimized operating conditions (Table 1). The comparison confirmed the lowest SD and CV values for n = 10, which was selected for further computations in the LepiSuite LEP Analyzer.

3.1.4 Application of optimized conditions and interference from matrix ions

The interfering effect due to the matrix ions (Li^+, Na^+, K^+, Mn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, Br^-, NO_2^-, NO_3^-, and SO_4^{2-}) during the Pb analysis with LEP-OES at optimized measurement conditions has been checked (Figure 3). An assorted combination of anions and each cation were spiked with Pb in 0.1 mol L^{-1} HNO_3 to prepare an approximately 1:1 (5 μg mL^{-1}) mix. The results indicated a significant interfering impact for Mn^{2+} in the matrix.

The changes in the emission intensity for Pb (3 μg mL^{-1}) in 0.1 mol L^{-1} HNO_3 at λ_{max} = 405.8 nm in the spectra as obtained using the optimized LEP-OES parameters vs. the default conditions is shown in Figure 4. The optimized conditions produced a clear emission peak for Pb, which is also distinct from the background peaks.

3.2 Selective preconcentration of lead using MRT-SPE

3.2.1 Retention behavior in terms of pH

The solution pH has a substantial impact on the retention efficiency of target analytes in SPE systems [40, 41]. The comparative retention of Pb and Mn in MRT-SPEs, Pb-01, Pb-02 and Pb-04, were studied as a function of pH. The solution pH was varied between 1 and 8, with at least one pH unit interval, as maintained using HNO_3 and appropriate buffers (MES, HEPES or TAPS). The quantitative selectivity towards Pb from a mixed solution of Pb and Mn (1:1; 5 μg mL^{-1} Pb or Mn) as well as maximum retention was observed both with Pb-01 (up to pH 2) and Pb-02 (pH 1 to 4), while Pb-04 was unavailable to perform the task (Figure 5). The geochemical changes, such as a drop in Eh or an increase in pH significantly affect Pb-mobility in the natural environment [42]. In a reacting geochemical system, the metal ions usually remain in solution as long as the pH is below 3.5 while sorption of dissolved Pb onto hydrous ferric hydroxide at pH <4 might occur as well [42, 43]. Therefore, to avoid any risk of precipitation, the sample solution pH was maintained at pH ~1 and the MRT-SPE systems were also conditioned to the same pH during the following experiments. The content of selectively retained Pb (%) at pH ~1 was 99.8 ± 0.3 in Pb-01 and 100 ± 0.4 in Pb-02, which were considered for further experiments.

3.2.2 Effect of washing solvents

A washing step using a solvent of low elution strength is often involved after the sample loading step to eliminate the unwanted matrix components without displacing the target analytes [31, 32]. Such a step is crucial to SPE operations to minimize impacts of the residual matrix that could affect the measurement accuracy of the target analyte [34]. The mechanism of selective retention in an SPE depends on several factors [36, 44, 45], and a pH-dependent Pb-retention behavior in Pb-01 or Pb-02 has been observed. The ultrapure water induced washing resulted in a back-extraction of about 5 ± 0.7 Pb (%), while it turned out to be zero or below detectable limit with 0.01 M HNO_3. The behavior is attributable to the higher pH of ultrapure water (pH ~5 or more) than the HNO_3. Thus, 0.01 M HNO_3 is used as the washing solvent in next steps.

3.2.3 *Recovery of analytes with eluent*

Elution achieves the recovery of retained analytes from the SPE systems, and the eluent is selected based on several factors, e.g., required volume be minimum, no impact on the after-elution measurements of a target analyte, and so forth [46]. The aminopolycarboxylate chelators, EDTA or nitrilotriacetic acid (NTA) (0.03 mol L^{-1}) is a recommended eluent for Pb-01, Pb-02, and Pb-04, while acids (≥1 mol L^{-1}) that can solubilize Pb (excluding aqua regia) is also a proposed option to use with Pb-04 [47]. In the current work, EDTA ($\log K_{Pb\text{-}EDTA}$ = 18.0) is preferred over NTA ($\log K_{Pb\text{-}NTA}$ = 11.48) due to the higher stability of the corresponding Pb-complexes (I = 0.1 mol·dm^{-3}; T = 25 ± 0.1°C) [48]. Several other solvents, other than EDTA (0.03 mol L^{-1} solution of EDTA-4Na), have also been evaluated for the desorption of retained Pb at pH ~1, which are HCl, HNO_3, NaOH (1 mol L^{-1}), and an EDTA + HNO_3 mixed solution (0.03:0.001, mol L^{-1}). A better recovery rate (%) with EDTA (0.03 mol L^{-1}) was achieved compared to the other eluents (Figure 6a).

The effect of solution pH on the elution of retained Pb at pH ~1 with 0.03 mol L^{-1} EDTA was evaluated in the range of pH 3 to 10. The incomplete solubility of EDTA in the aqueous medium at very low pH [49] limited the implementation of pH below 3, while the solubilization possibility of silica gel base support of MRT-SPEs [50] restricted the use of pH above 10. A quantitative recovery rate (%) at pH ≥ 9 were obtained for both Pb-01 and Pb-02 MRT-SPEs (Figure 6b), and an eluent pH of 10 were maintained in further investigations.

The volume of eluent consumed to recover the retained analyte quantitatively from the MRT-SPEs reciprocally affects the overall enrichment factor [51]. A minimum volume of 6 mL (EDTA, 0.03 mol L^{-1}; pH 10) was required for the complete recovery of retained Pb from Pb-01, while 3 mL was used in Pb-02 (Figure 6c). Hence, Pb-02 was assumed to be economical among the MRT-SPE systems in terms of the eluent volume consumption.

3.2.4 *Effect of flow-rates*

The flow-rates of sample and eluent loading is an important factor to regulate the efficiency in the SPE-assisted quantitative separation of analytes [27, 40, 52]. The flow-rates were, therefore, varied within the range of 0.3 to 10 mL min^{-1} using stopcock-equipped flow-rate controllers for selective Pb separation using Pb-01 and Pb-02 MRT-SPE systems, while other parameters have been maintained as optimized (Figure 7). The retention and recovery rates of

Pb were quantitative for sample and eluent flow rates up to 0.5 mL min^{-1} followed by a gradual decrease after that. Hence, an optimal flow-rates below 0.5 mL min^{-1} was maintained in both initial sample-loading and elution steps during further experiments.

3.2.5 Retention capacity and reusability

The retention capacity is a measure of the stability of an SPE system during a separation process, which can be calculated using the analyte content in a solution and the breakthrough volume (BV) for that solution [53]. The BV is defined as the volume of sample that causes the analyte of interest to be eluted from the SPE system. Standard aliquots of Pb solutions (6 to 200 mL; 0.02 mmol L^{-1}) were passed through the Pb-01 and Pb-02 mini-columns under optimized conditions, eluted and analyzed to estimate the retention capacity, and expressed in terms of millimoles of analyte retained in per gram of MRT-SPEs (Figure 8). A quantitative sorption (>98%) was obtained for sample volumes up to 120 and 162 mL, respectively, in Pb-01 and Pb-02, which corresponds to the 0.12 and 0.14 mmol g^{-1} of retention capacities. A higher retention capacity of Pb-02 than Pb-01 can be noted, and thereby assumed as a superior option for next experimental segments.

The regeneration ability of an SPE system facilitates its repeated use and improves the process economics [54]. The Pb-02 MRT-SPE system was checked for reusability, and it sustained for more than 100 retention-elution cycles without the loss of analytical performance.

3.2.6 Effect of coexisting ions in matrices

The common coexisting ions often hamper the selectivity towards an ion within an SPE system in aqueous matrices [55, 56]. The selectivity of Pb-02 MRT-SPE towards Pb in the presence of Mn and other cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) or anions (Cl^-, Br^-, NO_2^-, NO_3^-, and SO_4^{2-}) in solutions were checked. Model solutions containing 5 µg mL^{-1} each of Pb and Mn were spiked with varying concentrations (0.001 to 1.0 mol L^{-1}) of different cations and anions and treated in Pb-02 SPE system at optimized conditions. An optimum tolerable concentration ratio (ion: Pb = 4×10^4) was computed in the presence of Li^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, NO_2^-, NO_3^-, and SO_4^{2-} ions in mixtures, while it is reduced by 10 times for K^+ and Sr^{2+} (ion: Pb = 4×10^3) and 1000 times for Ba^{2+} (ion: Pb = 0.4×10^2). Although K^+ occurs widely in the environment, including all natural waters [57], the Sr^{2+} and

Ba^{2+} occur in trace quantities [58, 59]. Hence, the major ions in aqueous matrices seem to have minimum impact on the selective separation of Pb.

3.2.7 Preconcentration factor

The preconcentration step is included within an analytical protocol when the analyte concentration in a sample is lower than the detection limit of the instrument, and it can be achieved by increasing the ratios of sample to eluent volumes [54]. The retained analytes from different sample volumes (20 to 560 mL; 0.1 μg mL^{-1} Pb) in Pb-02 SPE system were eluted using 3 mL of 0.03 mol L^{-1} EDTA (pH 10). The Pb-recovery rate was 96.2% from the final solution to indicate a preconcentration factor of 187 (RSD: relative standard deviation, <4.5%).

3.3 MRT-SPE/LEP-OES analysis for Pb

3.3.1 Scheme for on-site analysis

The protocol for on-site Pb analysis in an aqueous matrix using LEP-OES included two operating segments, which started with the selective separation/preconcentration in the Pb-02 MRT-SPE and followed by analysis using LEP-OES. The LEP-OES system is portable and capable of on-site analysis, while the MRT-SPE has been modified to the micro-column format to fit the scheme. The powdered mass of Pb-02 MRT-SPE (20 mg) was packed in micropipette tips, and the sample loading or elution at a controlled flow-rate was performed using the syringe-type simple reciprocating pump. The volume of eluent (0.03 mol L^{-1} EDTA, pH 10) was proportionately reduced to 100 μL to match with that of SPE-mass. The elution effluent was fortified with 3 mol L^{-1} HNO_3 (10 μL) to adjust the solution pH ≤ 1 before the LEP-OES analysis. A schematic of the complete operating protocol is shown in Figure 9.

On-field application of the protocol will require about 5 min without preconcentration, while the preconcentration step will add 25 min to the cumulative total. The measurement tools and the preconcentration assembly can be carried in a lightweight briefcase for on-site sample-to-answer analysis.

3.3.2 Analytical characteristics

The Pb-content in the aqueous matrix has been measured using LEP-OES combined with SPE separation and/or preconcentration at optimized operating conditions. The coefficient of

determination (R^2) for the range of 0 to 5 μg mL^{-1} Pb, after preconcentration of 0 to 0.025 μg mL^{-1} Pb using Pb-02 MRT-SPE and elution with 0.03 mol L^{-1} EDTA (0.1 mL), was 0.9989 and the linear equation was $y = 488.33x + 30.314$ (slope, 488.33; intercept, 30.314). The limits of detection (LOD) and limits of quantification (LOQ) for the method were calculated as the concentration corresponding to three and ten times of the standard deviation (SD, σ) value for 20 runs of the blank [60]. The LOD and LOQ values were, respectively, 1.9 and 6.5 ng mL^{-1} for the preconcentration with Pb-02 and LEP-OES combination. The comparison of LOD/LOQ values with and without the Pb-02 SPE showed an SPE-induced improvement in efficiency by about 20-times. The repeatability, as RSD, for the combination of LEP-OES and the SPE was lower than 5% calculated from 10 replicate measurements of 0.1 μg mL^{-1} Pb, indicate a good precision of the method for Pb-analysis in the aqueous matrix.

3.3.3 Accuracy and applications

The accuracy of the proposed analysis scheme was evaluated by analyzing wastewater CRMs: SPS-WW1 and ERM-CA713 (Table 3). The total Pb contents determined for both CRMs using LEP-OES were in good agreement with the certified values with the satisfactory recoveries of >96%. The proposed scheme was also applied to the analysis of local natural samples (tap, river and rain waters) as prepared following the standard addition method (Table 2). A reasonable consistency has been observed between the added and measured Pb concentrations in the natural water samples, and the recoveries were varied over the range of 95.1–96.7%. Furthermore, all the analysis results of LEP-OES were in good agreement with that of ICP-OES.

4.0 Conclusions

In this work, a method is proposed for the on-site analysis of aqueous samples for Pb contents using LEP-OES. The operating parameters were optimized to generate a distinguishable peak for Pb at λ_{max} = 405.8 nm in the LEP-OES spectra: acid concentration, 0.1 mol L^{-1} HNO_3; applied voltage, 950 v; on-time, 5 ms; off-time, 60 ms; pulse count for applied voltage, 90; number of measurements per spectra, 10. An SPE-assisted sample pre-treatment step was introduced for selective separation of Pb from the matrix and preconcentration of the target

analytes to enhance the detectable range of LEP-OES. The SPE-system used was Pb-02, which was selected among three options (Pb-01, Pb-02, and Pb-04) after comparative evaluation. The operating variables for selective quantitative separation of Pb from solution were optimized as follows: SPE-mass, 20 mg; pH, ≤1; washing solvent, 0.01 M HNO_3; eluent, 0.03 mol L^{-1} EDTA; eluent volume, 100 μL; flow-rates (sample-loading or elution), 0.5 mL min^{-1}. The proposed method combining LEP-OES and the SPE provided lower LOD and LOQ for Pb determination as 1.9 and 6.5 ng mL^{-1}. The accuracy of the LEP-OES measurement of Pb coupled with SPE separation/preconcentration was validated by analyzing certified reference materials (recovery rate: >96%), and the analysis result was also comparable with that of ICP-OES. The system was used to detect Pb in simulated real samples as an example of field applications to observe a fast-measurement time (sample-to-answer, without preconcentration, <5 min), and high sensitivity in analysis at ppb levels and below permissible range. The future research will focus on the extension and utility of this system for other challenging toxic elements.

Acknowledgement

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Table 1: Optimization of the number of measurements in a group per spectra in LEP-OES [a]

Emission intensity per spectrum	Mean of the number of measurements in a group			
	Mean of three	Mean of five	Mean of six	Mean of ten
1865.7	1923.2	1936.6	1942.8	2000.0
1988.8				
1915.1				
1917.2	1962.3			
1995.9				
1973.8		2063.4		
2091.5	2061.4		2032.3	
2096.6				
1996.1				
2158.9	2003.2			
1888.4		2011.5		2022.6
1962.2				
2121.8	2069.0		2047.2	
1987.8				
2097.4				
1973.3	2025.5	2033.7		
2092.9				
2010.1				
2019.1	2117.4		2096.6	
2072.8				
2260.3		2148.5		2127.2
2099.7	2075.9			
2005.3				
2122.7				
2254.3	2168.2		2130.7	
2170.3		2106.0		
2080.0				
2032.5	2093.2			
2111.4				
2135.7				
n	3	5	6	10
SD	73.1	74.3	71.6	67.9
CV	3.6	3.6	3.5	3.3

[a] Optimized operating conditions: applied voltage, 950 v; on-time, 5 ms; off-time, 60 ms; pulse count, 90 for Pb (3 μg mL^{-1}) in 0.1 mol L^{-1} HNO_3 at λ_{max} = 405.8 nm; *n* = number of measurements in a group per spectra; SD = Standard deviation; CV = Coefficient of variation

Table 2: Accuracy and application of the proposed method for lead analysis [a]

Sample name	Standard addition ($\mu g\ mL^{-1}$)	Certified value ($\mu g\ mL^{-1}$)	Pb content (without pre-concentration, $\mu g\ mL^{-1}$)		Pb content (after 100 fold preconcentration, $\mu g\ mL^{-1}$)		Recovery (%) of Pb (after 100 fold preconcentration)	
			ICP-OES	LEP-OES	ICP-OES	LEP-OES	ICP-OES	LEP-OES
SPS-WW1	0	0.1 ± 0.0005	0.1001 ± 0.0020	BDL	10.1 ± 0.32	9.69 ± 0.45	101.0 ± 3.18	96.9 ± 4.5
ERM-CA713	0	0.049 ± 0.0017	0.051 ± 0.0006	BDL	5.02 ± 0.41	4.72 ± 0.31	102.45 ± 4.12	96.32 ± 6.33
Tap water-1	0	–	0.0009 ± 0.0072	BDL	NA	NA	–	–
	0.1	–	0.1013 ± 0.0032	BDL	9.99 ± 0.13	9.73 ± 0.40	99.01 ± 1.29	96.05 ± 3.96
Tap water-2	0	–	0.004 ± 0.0079	BDL	NA	NA	–	–
	0.1	–	0.1037 ± 0.0065	BDL	10.41 ± 0.32	10.06 ± 0.42	100.09 ± 3.08	96.73 ± 4.04
River water	0	–	0.0028 ± 0.0019	BDL	NA	NA	–	–
	0.1	–	0.1038 ± 0.0020	BDL	10.27 ± 0.03	9.78 ± 0.34	99.90 ± 0.33	95.10 ± 3.30
Rain water	0	–	0.0066 ± 0.0058	BDL	–	–	–	–
	0.1	–	0.1054 ± 0.0031	BDL	10.57 ± 0.12	10.27 ± 0.41	99.16 ± 1.13	96.34 ± 3.94

[a] Optimized LEP-OES operating conditions: applied voltage, 950 v; on-time, 5 ms; off-time, 60 ms; pulse count, 90; n = 10 for Pb in 0.1 mol L^{-1} HNO_3 at λ_{max} = 405.8 nm; BDL, Below detectable limit; NA, Analysis not performed.

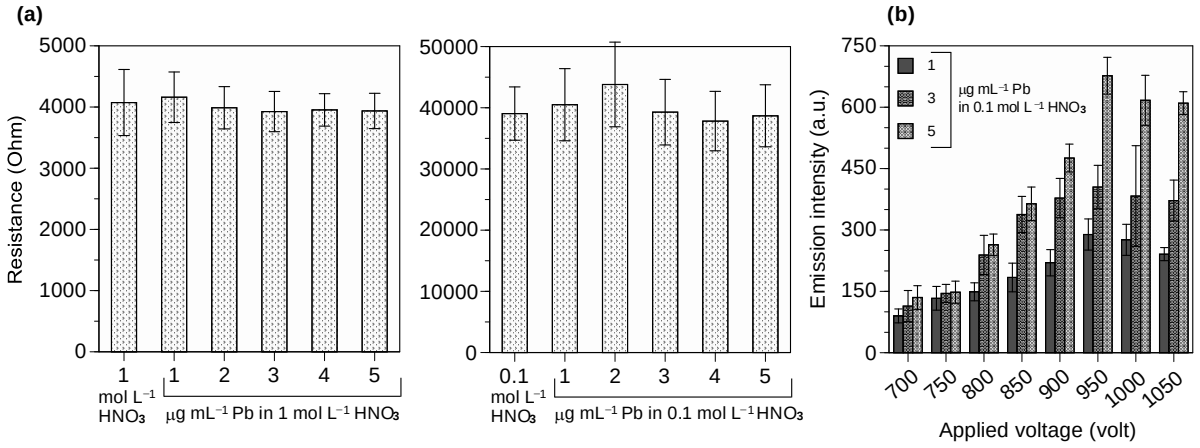

Figure 1: (a) Comparative resistance values for strong acids (0.1 and 1.0 mol L^{-1} HNO_3) vs Pb standards (1 to 5 μg mL^{-1}) in HNO_3 (voltage, 200 V; on-time, 2 ms; off-time, 40 ms; pulse count, 10; *n* = 10). (b) The peak intensity for Pb at λ_{max} = 405.8 nm (1, 3 and 5 μg mL^{-1} Pb in 0.1 mol L^{-1} HNO_3) at different applied voltage (750 to 1050 v) (on-time, 2 ms; off-time, 40 ms; pulse count, 40; *n* = 10).

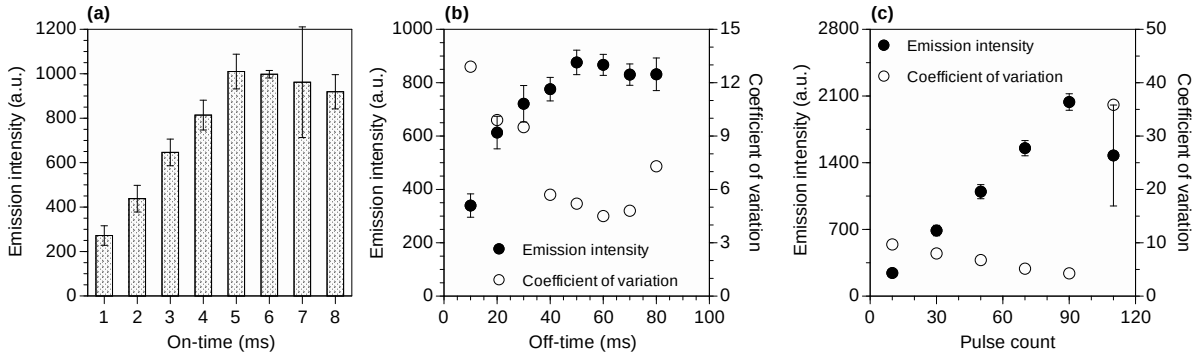

Figure 2: Effect of (a) on-time (applied voltage, 950 v; on-time, 1–8 ms; off-time, 40 ms; pulse count, 40), (b) off-time (applied voltage, 950 v; on-time, 5 ms; off-time, 10–80 ms; pulse count, 40), (c) pulse count for applied voltage on the emission peak intensity (applied voltage, 950 v; on-time, 5 ms; off-time, 60 ms; pulse count, 10–110) for Pb (3 μg mL^{-1}) in 0.1 mol L^{-1} HNO_3 at λ_{max} = 405.8 nm (n = 10).

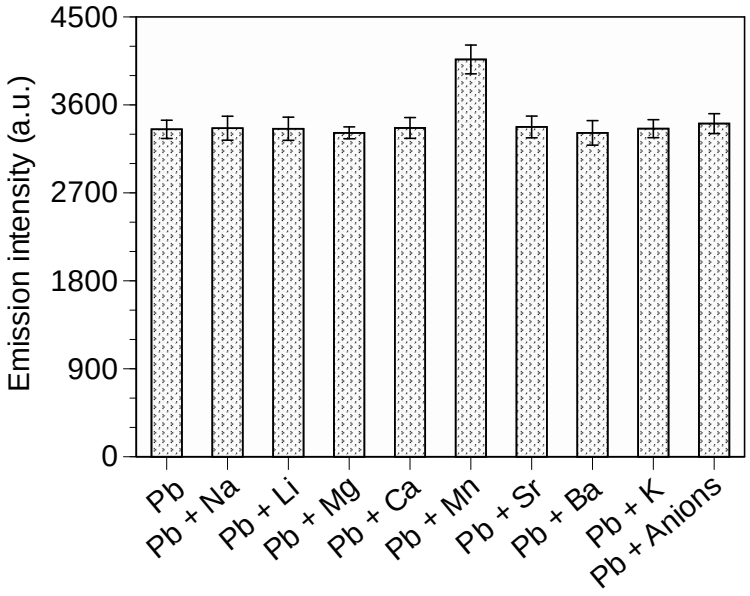

Figure 3: The interfering effects due to the matrix ions for the analysis of Pb (5 μg mL^{-1}) in 0.1 mol L^{-1} HNO_3 nm at optimized conditions (applied voltage, 950 v; on-time, 5 ms; off-time, 60 ms; pulse count, 90) (n = 10) prior to the pre-treatment with MRT-SPEs.

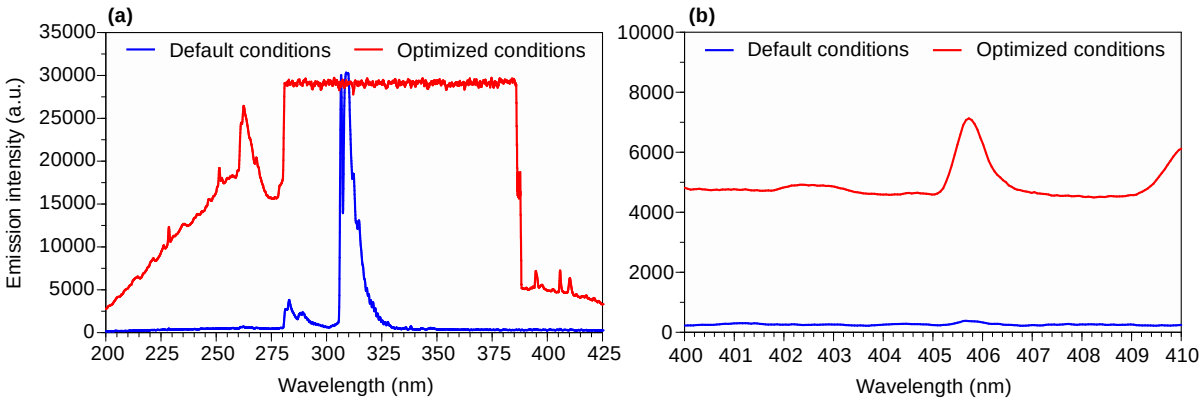

Figure 4: The differences in the spectra from LEP-OES (a. 200–425 nm; b. 400–410 nm) obtained for Pb (3 µg mL^{-1}) in 0.1 mol L^{-1} HNO_3 nm at default operating conditions (applied voltage, 750 v; on-time, 3 ms; off-time, 40 ms; pulse count, 40) and optimized conditions (applied voltage, 950 v; on-time, 5 ms; off-time, 60 ms; pulse count, 90) (n = 10).

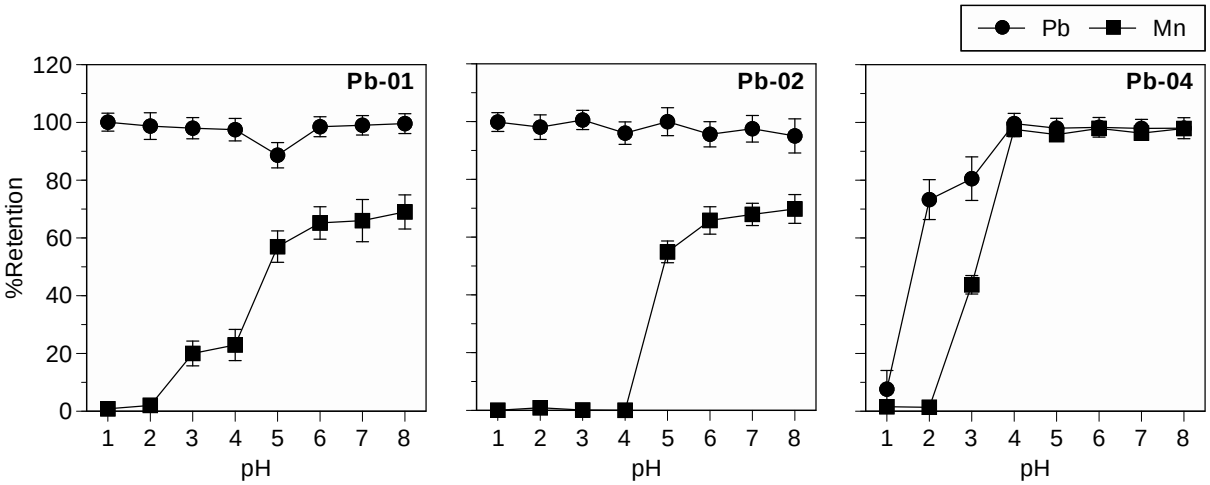

Figure 5: Comparative retention of Pb and Mn in the MRT-SPEs, Pb-01, Pb-02 and Pb-04, as a function of pH (n = 3). Sample solution, Pb:Mn (1:1, 5 μg mL^{-1}); matrix, H_2O; pH, 1–8; sample volume, 6 mL, conditioning solution, 0.01 mol L^{-1} HNO_3; flow rate, ≤ 0.5 mL min^{-1}.

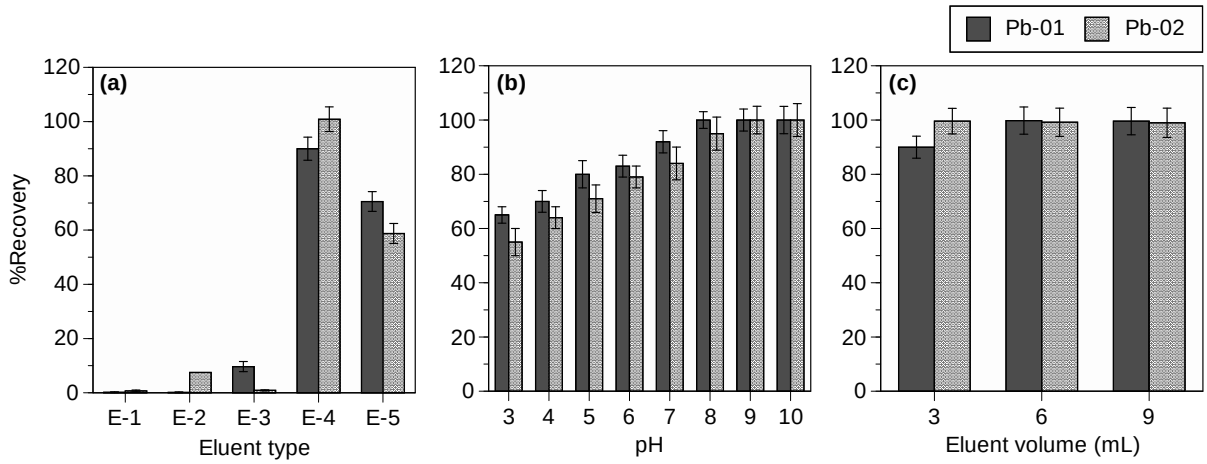

Figure 6: Recovery of Pb from the Pb-01 and Pb-02 MRT-SPEs (n = 3): (a) selection of eluent (E-1, 1 mol L^{-1} HCl; E-2, 1 mol L^{-1} NaOH; E-3, 1 mol L^{-1} HNO_3; E-4, 0.03 mol L^{-1} EDTA; E5, 0.03 mol L^{-1} EDTA in 0.001 mol L^{-1} HNO_3); (b) effect of eluent pH on the recovery rate (pH, 3–10); (c) selection of eluent volume (volume, 3–9 mL). Sample solution, Pb (5 μg mL^{-1}); matrix, H_2O; sample volume, 6 mL, conditioning solution, 0.01 mol L^{-1} HNO_3; flow rate, ≤ 0.5 mL min^{-1}.

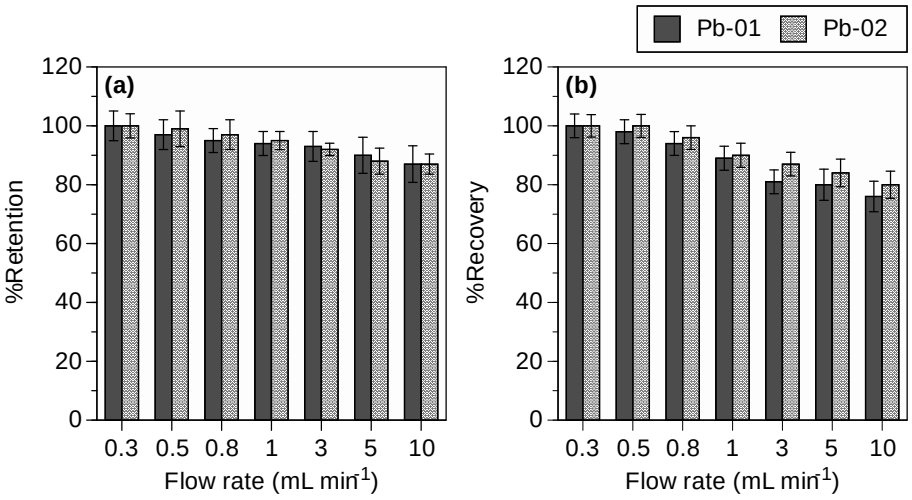

Figure 7: Effect of flow-rates on (a) retention and (b) elution of Pb from the MRT-SPEs, Pb-01 and Pb-02 (n = 3). Sample solution, Pb (5 µg mL^{-1}); matrix, H_2O; sample volume, 6 mL, conditioning solution, 0.01 mol L^{-1} HNO_3; flow rate, 0.3 to 10 mL min^{-1}.

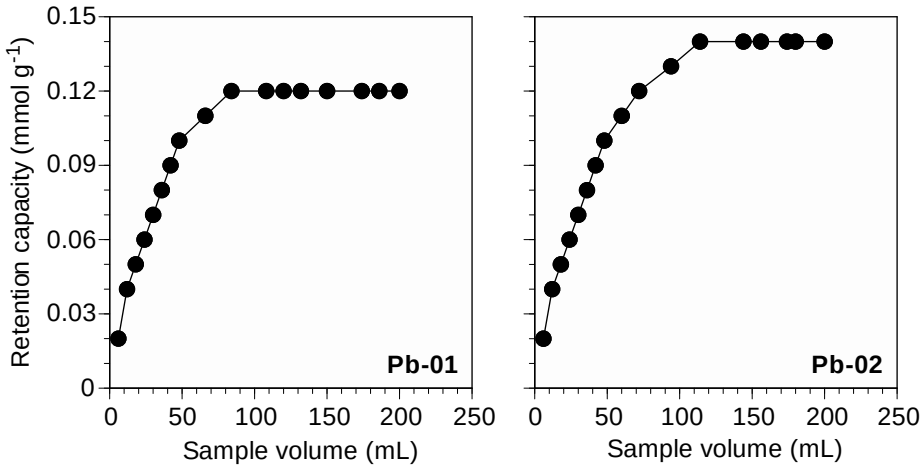

Figure 8: Capacity of Pb-retention in the MRT-SPEs, Pb-01 and Pb-02. Sample solution, Pb (0.02 mmol); matrix, H_2O; sample volume, 6–200 mL, conditioning solution, 0.01 mol L^{-1} HNO_3; flow rate, ≤ 0.5 mL min^{-1}.

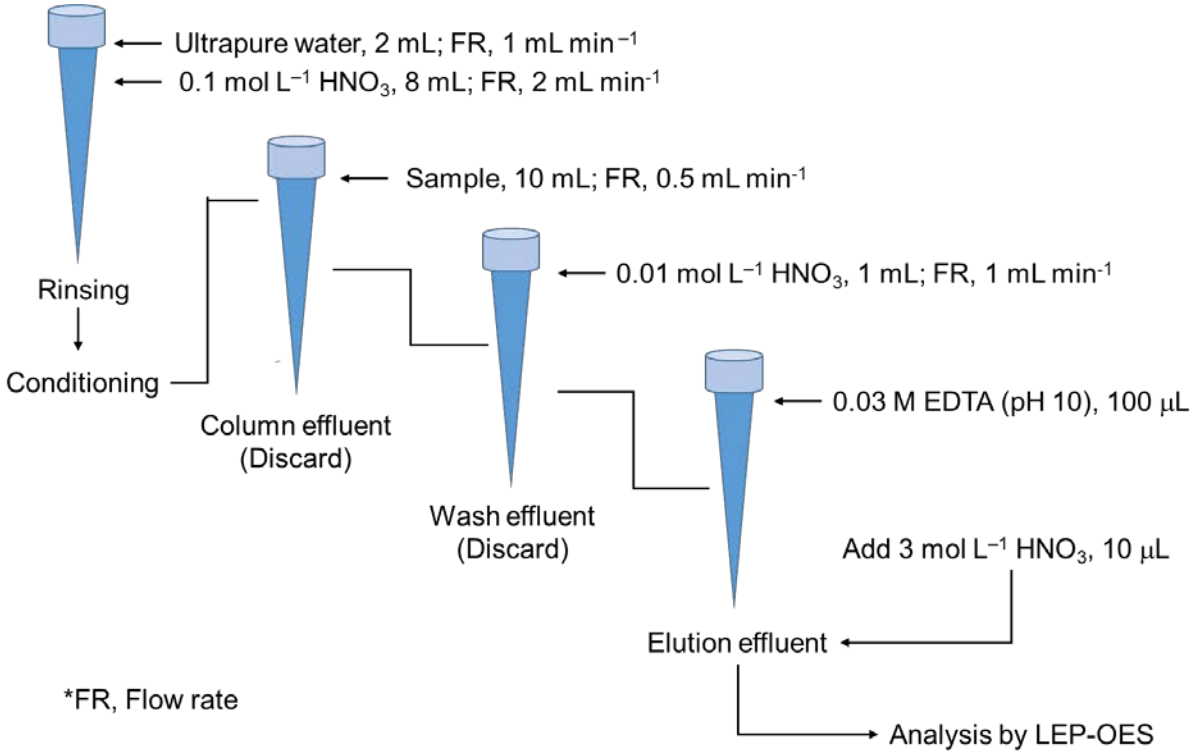

Figure 9: Scheme of the operating protocol for analysis of Pb using LEP-OES coupled with separation/preconcentration by Pb-02 MRT-SPE